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(71) 出願人 586062772

小沢 昭弥

愛知県一宮市千秋町浮野字湯受39-2

(71) 出願人 586115953

間瀬 俊三

愛知県海部郡飛島村大字飛島新田字元起之郷435

(72) 発明者 小沢 昭弥

愛知県一宮市千秋町浮野字湯受39-2

(72) 発明者 加藤 忠哉

三重県津市浅見町700-26

(72) 発明者 間瀬 俊三

愛知県海部郡飛島村大字飛島新田字元起之郷435番地

(54) 【発明の名称】 リチウムイオン電池およびその製造法

(57) 【要約】

【課題】 有機電解液を用いた電池の容器が破損した際に、電解液が流出し電池容器の破損に伴う両極の短絡によるジュール熱による発火事故を防止するリチウムイオン電池およびその製造法を提供する。

【解決手段】 ゲルの原料を含む溶液を両極間に含浸させて後熱重合させるか、電解液を含む高分子を予め両極間に存在させるか、あるいは高分子を予め両極間に存在させた後液を含浸させ膨潤させることによりゲル状の電解液とすることで、破損時の火災の危険性の少ないリチウムイオン電池を得る。

【特許請求の範囲】

【請求項1】正極および負極をそれぞれ箔状の集電体の表面に形成し、両者を互いに対向せしめた状態でらせん状に巻き、この両者間に有機溶媒と、ゲル化剤またはその原料とからなる液を含浸せしめ、これをゲル化させた後該ゲル中にリチウムを含む電解質を拡散させることを特徴とするリチウムイオン電池の製造法。

【請求項2】正極および負極をそれぞれ箔状の集電体の表面に形成し、両者を互いに対向せしめた状態でらせん状に巻き、この両者間にリチウムを含む電解質と、該電解質を溶解した有機溶媒と、ゲル化剤またはその原料とからなる電解液を含浸せしめ、これをゲル化させることを特徴とするリチウムイオン電池の製造法。

【請求項3】正極および負極をそれぞれ箔状の集電体の表面に形成し、更にそれらの表面または両極の間の介在するセパレーターの少なくとも一部にゲル化剤またはその原料を存在せしめ、前記正極および負極を互いに対向せしめた状態でらせん状に巻き、この両者間に有機溶媒を含浸せしめて前記ゲル化剤またはその原料を溶解し、この溶液をゲル化させた後該ゲル中にリチウムを含む電解質を拡散させることを特徴とするリチウムイオン電池の製造法。

【請求項4】正極および負極をそれぞれ箔状の集電体の表面に形成し、更にそれらの表面または両極の間の介在するセパレーターの少なくとも一部にゲル化剤またはその原料を存在せしめ、前記正極および負極を互いに対向せしめた状態でらせん状に巻き、この両者間にリチウムを含む電解質と、該電解質を溶解した有機溶媒とからなる電解液を含浸せしめて前記ゲル化剤またはその原料を溶解し、この溶液をゲル化させることを特徴とするリチウムイオン電池の製造法。

【請求項5】正極および負極をそれぞれ箔状の集電体の表面に形成し、更にそれらの表面または両極の間の介在するセパレーターの少なくとも一部に有機溶媒と高分子からなるゲルを存在せしめ、前記正極および負極を互いに対向せしめた状態でらせん状に巻き、この両者間にリチウムを含む電解質を含浸せしめることを特徴とするリチウムイオン電池の製造法。

【請求項6】正極および負極をそれぞれ箔状の集電体の表面に形成し、更にそれらの表面または両極の間の介在するセパレーターの少なくとも一部に有機溶媒と、高分子と、リチウムを含む電解質とからなるゲルを存在せしめ、前記正極および負極を互いに対向せしめた状態でらせん状に巻くことを特徴とするリチウムイオン電池の製造法。

【請求項7】ゲル化が熱重合反応で起こる請求項1ないし請求項6のいずれかに記載のリチウムイオン電池の製造法。

【請求項8】ゲル化が付加重合反応、重付加反応、開環重合反応、重縮合反応のいずれかの反応によって2官能

性モノマーと多官能性モノマーからなる分岐あるいは架橋高分子の生成によって起こる請求項1ないし請求項6のいずれかに記載のリチウムイオン電池の製造法。

【請求項9】ゲルを構成する高分子がポリアクリル酸メチル、ポリメタクリル酸メチル、ポリアクリロニトリル、ポリスチレン、ポリ酢酸ビニル、ポリケイ皮酸ビニル、環化ゴム、ポリシラン、ポリシロキサン、エポキシ化ポリブタジエン、ポリエーテル、ポリウレタン、ポリエステルおよびそれらの共重合体の中の少なくとも1つを含む請求項1ないし請求項6のいずれかに記載のリチウムイオン電池の製造法。

【請求項10】ゲルを構成する高分子とその中に含まれる有機溶媒との溶解性パラメーターの比が1対0.7ないし1対1.3の範囲内である請求項1ないし請求項6のいずれかに記載のリチウムイオン電池の製造法。

【請求項11】正極および負極がそれぞれ箔状の集電体の表面に形成され、両者が互いに対向した状態でらせん状に巻かれており、この両者間に熱重合反応で生成したゲル状電解液が介在し、該ゲル状電解液中にはリチウムを含む電解質と、該電解質を溶解した有機溶媒とが含まれていることを特徴とするリチウムイオン電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明はリチウムイオン電池およびその製造法に関し、特に安全性と耐久性に優れた新規な電解液を用いたリチウムイオン電池およびその製造法に関するものである。

【0002】

【従来の技術】リチウムイオン電池はそのエネルギー密度が高いことから、携帯用電子機器の電源として盛んに使われており、更に電気自動車用の電源としても開発が進められている。この種の電池では、負極にはリチウムのインターカーレーションの起こるカーボンを用い、正極にはCo、Ni、Mn等の酸化物とリチウムとの複合酸化物を用い、この間に多孔質の膜状のセパレーターを挟み、この3者を有機溶剤であるエチレンカーボネート等に電解質であるLiPF₆等を溶かした電解液中に浸した構成になっている。しかしながら、この電池は可燃性の有機溶媒を電解質の溶剤として用いており、電池が破損したり、シールが不完全で有ったりした場合には、この有機溶媒が容器の外に流出して引火し、火災になる危険性がある欠点があった。

【0003】また、電池の充放電に伴い、正極物質や負極物質が僅かに体積変化を起こし、これに伴い両極間に空隙が生じたり、セパレーターの目詰まりを生じたりして電池の容量や内部抵抗が劣化する問題があった。

【0004】有機溶媒の代わりにイオン伝導性のポリマーのシートを両極間のセパレーターとして用いるいわゆるポリマー電池が開発されているが、電極活物質との接

触が不十分となるために内部抵抗が高い、セパレーターの体積が余分に必要となる等の欠点があった。

【0005】

【発明が解決しようとする課題】本発明は、かかる問題点に鑑み、電池が破損した場合でも有機溶媒が容器の外に流出する可能性が小さく、従って安全性が高く、且つ充放電に伴う劣化が少なく、体積エネルギー密度の大きいリチウムイオン電池を提供することを目的とする。

【0006】

【課題を解決するための手段】本発明は、(1)正極および負極をそれぞれ箔状の集電体の表面に形成し、両者を互いに対向せしめた状態でらせん状に巻き、この両者間に有機溶媒と、ゲル化剤またはその原料とからなる液を含浸せしめ、これをゲル化させた後該ゲル中にリチウムを含む電解質を拡散させるリチウムイオン電池の製造法、および、(2)正極および負極をそれぞれ箔状の集電体の表面に形成し、両者を互いに対向せしめた状態でらせん状に巻き、この両者間にリチウムを含む電解質と、該電解質を溶解した有機溶媒と、ゲル化剤またはその原料とからなる電解液を含浸せしめ、これをゲル化させるリチウムイオン電池の製造法、および、(3)正極および負極をそれぞれ箔状の集電体の表面に形成し、更にそれらの表面または両極の間の介在するセパレーターの少なくとも一部にゲル化剤またはその原料を存在せしめ、前記正極および負極を互いに対向せしめた状態でらせん状に巻き、この両者間に有機溶媒を含浸せしめて前記ゲル化剤またはその原料を溶解し、この溶液をゲル化させた後該ゲル中にリチウムを含む電解質を拡散させるリチウムイオン電池の製造法、および、(4)正極および負極をそれぞれ箔状の集電体の表面に形成し、更にそれらの表面または両極の間の介在するセパレーターの少なくとも一部にゲル化剤またはその原料を存在せしめ、前記正極および負極を互いに対向せしめた状態でらせん状に巻き、この両者間にリチウムを含む電解質と、該電解質を溶解した有機溶媒とからなる電解液を含浸せしめて前記ゲル化剤またはその原料を溶解し、この溶液をゲル化させるリチウムイオン電池の製造法、および、

(5)正極および負極をそれぞれ箔状の集電体の表面に形成し、更にそれらの表面または両極の間の介在するセパレーターの少なくとも一部に有機溶媒と高分子からなるゲルを存在せしめ、前記正極および負極を互いに対向せしめた状態でらせん状に巻き、この両者間にリチウムを含む電解質を含浸せしめるリチウムイオン電池の製造法、および、(6)正極および負極をそれぞれ箔状の集電体の表面に形成し、更にそれらの表面または両極の間の介在するセパレーターの少なくとも一部に有機溶媒と、高分子と、リチウムを含む電解質とからなるゲルを存在せしめ、前記正極および負極を互いに対向せしめた状態でらせん状に巻くリチウムイオン電池の製造法、および、(7)正極および負極がそれぞれ箔状の集電体の

表面に形成され、両者が互いに対向した状態でらせん状に巻かれており、この両者間に熱重合反応で生成したゲル状電解液が介在し、該ゲル状電解液中にはリチウムを含む電解質と、該電解質を溶解した有機溶媒とが含まれており、リチウムイオン電池である。

【0007】(1)の方法は電解質による重合反応の妨害を考慮する必要が無く、ゲルの種類の選択範囲が比較的広く、良好な特性のゲルを得やすいが、工程が複雑となり、且つ、電解質の含浸に長時間を要する。(2)の方法はゲルの選択範囲が狭いが従来の製造工程を少し変更するだけで生産が可能であり、生産性が高い。(3)および(4)の方法はゲル化剤の原料溶液が高粘度の場合に特に有効であり、均一な濃度のゲルを短時間で作ることかできる。(5)および(6)の方法はゲルの分布が最も均一となり、品質のばらつきの少ない電池が得られるものである。

【0008】ゲル状の電解液の製法としては、熱重合反応を使うのが、製造工程の容易さや製品の破損事故の際のゲルの安定性の点で望ましく、例えばエチレンカーボネートを溶媒として、ビニルカルボネートとアゾビスイソブチロニトリルを溶解し、これを正極物質、負極物質、およびセパレーターの巻回品に減圧して含浸せしめ、窒素雰囲気中で60℃、20時間塊重合反応を行わせる。これにより、エチレンカーボネートを含んだ両極およびセパレーターの微細な孔の中まで充填する様に生成する。この後、電解質のLiPF₆を溶かしたエチレンカーボネート溶液中の浸して拡散せしめることにより電解質を含んで両極間を充填したゲルが得られることになる。また、予め電解質を溶解した非水系溶媒にモノマーと重合開始剤を溶解して反応させても良い。

【0009】熱重合によるゲル化反応は組み立てた電池の温度を制御することにより容易に制御することが出来る。たとえば、ビニル型モノマーおよびビニル型マクロモノマーを用いる溶液重合では反応の完結に必要な時間は次のとおりである。ここでマクロモノマーとは別名反応性オリゴマーと呼ばれ、その分子量が数千ダルトンである。多様な化学構造の設計により目的に応じた溶解性、ゲルの物性の制御を行うことができる。一方、マクロモノマーのゲル化の反応性はモノマーの反応性とほぼ同じであり、熱重合が可能である。

(1)開始剤としてAIBNを使用した場合。

50℃	74時間
70℃	4.8時間
100℃	7.2分

(2)開始剤としてラウリルパーオキシドを使用した場合。

50℃	47.7時間
70℃	3.5時間
100℃	3.5分

このように、温度制御によってゲル化の時間を制御でき

るので、製造工程に最適な条件が設定できる。

【0010】本発明で用いる重合反応として、反応の機構としては、付加重合反応、重付加反応、開環重合反応、重縮合反応のいずれかの反応によって2官能性モノマーと多官能性モノマーからなる分岐あるいは架橋高分子の生成によって起こる重合反応を好適に用いることができる。

【0011】また、本発明でゲルを構成する高分子としては、ポリアクリル酸メチル、ポリメタクリル酸メチル、ポリアクリロニトリル、ポリスチレン、ポリ酢酸ビニル、ポリケイ皮酸ビニル、環化ゴム、ポリシラン、ポリシロキサン、エポキシ化ポリブタジエン、ポリエーテル、ポリウレタン、ポリエステルおよびそれらの共重合体の中の少なくとも1つを含むものを好適に用いることができる。

【0012】本発明では、ゲルを構成する溶媒と高分子との溶解性パラメーター(δ)が近似していることが、良好なゲルを得るうえで望ましい。即ち、溶解性パラメーターの近いあるいは同じ高分子と溶媒の組み合わせでは、その溶媒が高分子を溶解する機能が最も優れており、そのような溶媒を良溶媒と呼ぶ。良溶媒はゲルを最大に膨潤させる。実在の高分子および溶媒の溶解性パラメーターのデータベースはほぼ完成しており、新規物質の δ 値を推定する方法も確立している。したがって、ゲルを最大に膨潤させる有機電解液を探索することが可能である。膨潤したゲル内のリチウムイオンの移動度は有機電解液のみの値にほぼ等しい。したがって、ゲルの存在によるイオン伝導度変化はゲル/良溶媒系では無視できる。ゲルを構成する高分子とその中に含まれる有機溶媒との溶解性パラメーターの比は1対0.7ないし1対1.3の範囲内であることが良好なゲルを得るうえで望ましく、更に1対0.8ないし1対1.2の範囲内であることがより望ましい。良溶媒の例としては、高分子がポリスチレン($\delta=18.7 \text{ MPa}^{1/2}$)、ポリメタクリル酸メチル($\delta=18.6 \text{ MPa}^{1/2}$)、ポリ酢酸ビニル($\delta=19.6 \text{ MPa}^{1/2}$)の場合、その良溶媒はテトラヒドロフラン($\delta=19.4 \text{ MPa}^{1/2}$)、ジエチルカーボネイト($\delta=18.0 \text{ MPa}^{1/2}$)である。

【0013】ゲルを予め電極の表面に薄く形成した後、巻回する方法として、例えば、各種アクリレートおよびメタクリレートモノマーの1種類あるいは複数のモノマーとビニレンカーボネイトモノマーの混合物をAIBNを開始剤としてDMF溶媒を用いて共重合して、生成物をメタノールで沈殿させて、2元あるいは多元共重合体を固体状で得る。この共重合体を有機電解質に膨潤・分散させてゲルを得る。このゲルは高いずり応力の元では会合構造が破壊されて良好な流動性を示す粘調な溶液となる。この溶液を電極上にドクターブレードを用いて薄膜状に塗布する。塗膜はゲル状態に戻る。こうして出来

た電極を巻回してゲル状電解液を有する電池とすることができる。

【0014】本発明に用いる正極物質や負極物質は電池の要求性能に応じて適宜選択することが可能であり、例えば、正極物質としてはMn、Ni、Fe等の遷移金属を主成分とし、リチウム、酸素からなる、充電・放電時にリチウムを脱離・吸蔵するリチウム複合金属酸化物を使用できる。

【0015】

【実施例】

【第一の実施例】 LiCoO_2 をアルミニウム箔に塗布し、プレス加工した正極と、グラファイトを銅箔に塗布し、プレス加工した負極とを多孔質のポリエチレン層を介してらせん状に巻き、有底円筒状の電池缶に装着した。この両極間に、メチルメタクリレートモノマーとビスフェノールAのジアリルカーボネイトモノマーとの重量比2対1からなるモノマー混合物を1Mの LiBF_4 を溶解したプロピレンカーボネイトと1,2ジメトキシエタンからなる混合有機溶媒に溶解して12%重量濃度の溶液とし、この溶液にAIBNをモノマー総重量当たり1.5%を添加した液を、減圧下で含浸せしめた。これを窒素ガス雰囲気下で封口し、75°Cにて30分間加熱してゲル状電解質を有するリチウムイオン電池を得た。

【0016】

【第二の実施例】 LiCoO_2 をアルミニウム箔に塗布し、プレス加工した正極と、グラファイトを銅箔に塗布し、プレス加工した負極とを多孔質のポリエチレン層よりなるセパレーターを介してらせん状に巻き、有底円筒状の電池缶に装着した。この両極間に、ポリスチレンモノマー180g、ジビニルベンゼン5g、ベンゼンパーオキシド1.5g、をテトラヒドロフラン150gに溶解した溶液を減圧下で含浸せしめた後、窒素雰囲気中で60°Cにて2時間加熱して重合反応をおこなわせた。これを窒素雰囲気下で1Mの LiPF_6 をエチレンカーボネイトとジメトキシエタンとの混合液に溶解した溶液を加えて膨潤させ、良好なゲル状電解液とし、封口し、リチウムイオン電池を得た。

【0017】

【第三の実施例】 LiCoO_2 をアルミニウム箔に塗布し、プレス加工した正極と、グラファイトを銅箔に塗布し、プレス加工した負極と、多孔質のポリエチレン層からなるセパレーターとに、酢酸ビニル100g、ケイ皮酸ビニル10g、AIBN2gをテトラヒドロフラン150gに溶解した液を、減圧下で含浸せしめた。これらをそれぞれ液から取り出し、窒素ガス雰囲気下で60°Cにて30分間加熱してゲルとした。この様にして得たゲルが空隙中に充填された正極、セパレーター、負極を巻回し、有底円筒状の電池缶に装着した。この両極間に、窒素雰囲気下で1Mの LiPF_6 をエチレンカーボ

ネイトとジメトキシエタンとの混合液に溶解した溶液を加えてゲル中に拡散させ、良好なゲル状電解液とし、封口し、リチウムイオン電池を得た。

【0018】

【第四の実施例】スチレンモノマー100g、ジビニルベンゼン2.5g、を乳化剤1gと過硫酸カリウム1gを含む水1リットルに分散させ、60°Cで1時間攪拌してポリスチレンラテックスを得る。このラテックスを凍結乾燥して粉末状とした後、ポリスチレンの良溶媒であるクロロホルムあるいはジメチルホルムアミドに分散させて膨潤マイクロゲルを得た。このマイクロゲルを三酸化イオウイオウによって表面スルホン化（スルホン化度0.1～15%）を行った。マイクロゲルは回収後水に分散させ、LiOHで完全に中和した後凍結乾燥してマイクロゲル粉末を得た。こうして得た表面スルホン化マイクロゲル粉末を、1MのLiPF₆のエチレンカーボネート、メチルエチルカーボネート（体積比1:3）溶液にて膨潤させてゲルとし、このゲルを正極、セパレーター、負極のそれぞれの表面に薄く塗布し、それぞれを重ねてらせん状に巻き、有底円筒状の電池缶に装着した。これを窒素雰囲気中で封口し、リチウムイオン電池を得た。

【0019】

【第五の実施例】メタクリレート200gとジビニルベンゼン1gに過酸化ベンゾイル1gを300mlの有機電解液で希釈して、60°C、3時間攪拌して高分子溶液を得た。これを両極の表面に薄膜状に塗布し、多孔質プラスチックスペーサーを挟んで巻回して、有底円筒状の電池缶に装着した。これを窒素雰囲気中で封口し、リチウムイオン電池を得た。

【0020】

【第六の実施例】LiCoO₂をアルミニウム箔に塗布し、プレス加工した正極と、グラファイトを銅箔に塗布し、プレス加工した負極とを多孔質のポリエチレン層よりなるセパレーターを介してらせん状に巻き、有底円筒状の電池缶に装着した。この両極間に、スチレンモノマー10ml、アクリレートまたはメタクリレートモノマー10mlの混合物とジビニルベンゼン1mlを有機電解質100mlに加え、ジクミルペルオキシド60mlを混合した溶液を浸透させた。これを70°Cで3時間熱処理することにより、重合反応を行わせた結果、浸透した溶液は濃厚高分子溶液となり、流動性が著しく低減した。

【0021】

【第七の実施例】ポリビニルアルコール0.5gを熱湯30mlに溶解した後500mlに希釈し、この溶液にスチレンモノマー15g、ジビニルベンゼン2g、過酸化ベンゾイル0.2gを加え、90°Cにて4時間攪拌してラテックス粒子を得た。この粒子をテトラヒドロフランにて膨潤させ、有機電解液にて分散させてスラリー状としたものをリチウムイオン電池の両極の表面に塗布し、巻回して電池とした。

【0022】

【発明の効果】第一ないし第四の実施例で作成した電池について、円筒状の電池の側面から釘をさしこむ破壊試験（釘さし試験）を行った。その際の状況は表1に示す様に、本発明の方法で作った電池では炎の発生は極めて小さいか認められず、これに対して電解質にゲルを使わなかった電池では電解液が流出し大きな炎となった。

【0023】

【表1】

試験品	釘さし試験の結果	
	炎の状態	電解液の流出
第一の実施例の電池	炎無し	無し
第二の実施例の電池	小さな炎(3cm)で5秒間	無し
第三の実施例の電池	小さな炎(3cm)で3秒間	無し
第四の実施例の電池	炎無し	無し
従来品(比較例)	大きな炎(30cm)で20秒以上	有り

【0024】以上の説明から明らかな通り、本発明によ

れば、両極の巻回品に電解液を含浸させた後、該電解液

をゲル状とするか、両極の表面に電解液を含んだゲルを存在せしめて巻回するか、あるいは両極の巻回品中に存在するゲルに電解質を含浸させることにより、電池の容

器が破損した際の電解液の流出が殆ど無い為、安全性に優れ、且つ充放電に伴う劣化も少ないリチウムイオン電池が得られるものであり、産業上極めて有用である。

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(21)Application number : 08-282830 (71)Applicant : OZAWA TERUYA
MASE SHUNZO

(22)Date of filing : 17.09.1996 (72)Inventor : OZAWA TERUYA
KATO TADAYA
MASE SHUNZO

(54) LITHIUM ION BATTERY AND MANUFACTURE OF IT

(57)Abstract:

PROBLEM TO BE SOLVED: To prevent the danger of fire generation by spirally winding first and second copper foil-like collectors each in which a positive electrode and a negative electrode are formed on the front surface so that the positive electrode faces the negative electrode, impregnating organic solvent and gelling agent between the positive electrodes and the negative electrodes, and diffusing electrolyte into gel.

SOLUTION: A positive electrode in which LiCoO_2 is applied to aluminum foil, and a negative electrode in which graphite is applied to copper foil are spirally wound through a separator composed of a porous polyethylene layer. Solution formed by dissolving polystyrene monomer, divinylbenzene, benzene peroxide in tetrahydrofuran is impregnated into a part between the positive electrode and the negative electrode, and polymerization reaction is performed. Solution formed by dissolving LiPF₆ in mixed liquid of ethylene carbonate and dimethoxy ethane and is added and swelled into gel-like electrolyte. Therefore, there is no possibility that organic solvent is allowed to flow to the outside of a container even if the battery is broken, and the danger of fire can be

prevented.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacturing method of the lithium ion battery characterized by diffusing the electrolyte which contains a lithium in this gel after forming a positive electrode and a negative electrode in the front face of a foil-like charge collector, respectively, winding spirally in the condition of having made both countering mutually, making the liquid which consists of an organic solvent, and a gelling agent or its raw material sink in among these both and making this gel.

[Claim 2] The manufacturing method of the lithium ion battery characterized by forming a positive electrode and a negative electrode in the front face of a foil-like charge collector, respectively, winding spirally in the condition of having made both countering mutually, making the electrolytic solution which consists of the electrolyte containing a lithium, an organic solvent which dissolved this electrolyte, and a gelling agent or its raw material sink in among these

both, and making this gel.

[Claim 3] Form a positive electrode and a negative electrode in the front face of a foil-like charge collector, respectively, and a gelling agent or its raw material is made to exist in a part of separator [at least] between which it is further placed between those front faces or two poles. The manufacturing method of the lithium ion battery characterized by diffusing the electrolyte which contains a lithium in this gel after having rolled said positive electrode and negative electrode spirally in the condition that you made it counter mutually, making an organic solvent sink in among these both, dissolving said gelling agent or its raw material and making this solution gel.

[Claim 4] Form a positive electrode and a negative electrode in the front face of a foil-like charge collector, respectively, and a gelling agent or its raw material is made to exist in a part of separator [at least] between which it is further placed between those front faces or two poles. The electrolyte which rolls said positive electrode and negative electrode spirally in the condition that you made it counter mutually, and contains a lithium among these both. The manufacturing method of the lithium ion battery characterized by making the electrolytic solution which consists of an organic solvent which dissolved this electrolyte sink in, dissolving said gelling agent or its raw material, and making this solution gel.

[Claim 5] The manufacturing method of the lithium ion battery characterized by forming a positive electrode and a negative electrode in the front face of a foil-like charge collector, respectively, making the gel which consists of an organic solvent and a macromolecule exist in a part of separator [at least] between which it is further placed between those front faces or two poles, winding spirally in the condition of having made said positive electrode and negative electrode countering mutually, and making the electrolyte containing a lithium sink in among these both.

[Claim 6] The manufacturing method of the lithium ion battery characterized by winding spirally in the condition of having formed the positive electrode and the negative electrode in the front face of a foil-like charge collector, respectively, having made the gel which consists of an organic solvent, a giant molecule, and an electrolyte containing a lithium existing in a part of separator [at least] between which it is further placed between those front faces or two poles, and having made said positive electrode and negative electrode countering mutually.

[Claim 7] The manufacturing method of a lithium ion battery according to

claim 1 to 6 from which gelation takes place at a thermal polymerization reaction.

[Claim 8] The manufacturing method of the lithium ion battery according to claim 1 to 6 which happens by generation of branching which gelation becomes from 2 functionality monomer and a polyfunctional monomer by one reaction of an addition polymerization reaction, a polyaddition reaction, a ring-opening-polymerization reaction, and a polycondensation reaction, or a crosslinked polymer.

[Claim 9] The manufacturing method of a lithium ion battery given in six to either claim 1 in which the giant molecule which constitutes gel contains at least one in polymethylacrylate, a polymethyl methacrylate, a polyacrylonitrile, polystyrene, polyvinyl acetate, Pori cinnamic-acid vinyl, cyclized rubber, polysilane, a polysiloxane, epoxidation polybutadiene, a polyether, polyurethane, polyester, and those copolymers thru/or a claim.

[Claim 10] The manufacturing method of the lithium ion battery according to claim 1 to 6 whose ratio of the soluble parameter of the macromolecule which constitutes gel, and the organic solvent contained in it is within the limits of 1 to 0.7 thru/or 1 to 1.3.

[Claim 11] The lithium ion battery characterized by making the electrolyte which a positive electrode and a negative electrode are formed in the front face of a foil-like charge collector, respectively, both are spirally rolled in the condition of having countered mutually, and the gel electrolytic solution generated at the thermal polymerization reaction intervenes among these both, and contains a lithium in this gel electrolytic solution, and the organic solvent which dissolved this electrolyte sink in.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to the lithium ion battery using the new electrolytic solution excellent in safety and endurance, and its manufacturing method about a lithium ion battery and its manufacturing method.

[0002]

[Description of the Prior Art] Since the energy density is high, it is

briskly used as a power source of a portable electronic device, and as for the lithium ion battery, development is furthered also as a power source further for electric vehicles. By this kind of cell, using the carbon with which INTAKARESHON of a lithium happens to a negative electrode, the separator of the shape of porous film is inserted into a positive electrode in the meantime using the multiple oxide of oxide, such as Co, nickel, and Mn, and a lithium, and it has composition dipped in the ethylene carbonate which is an organic solvent about these three persons into the electrolytic solution which melted the LiPF₆ grade which is an electrolyte. However, this cell used the inflammable organic solvent as an electrolytic solvent, when a cell was damaged or there was a seal by being imperfect, this organic solvent flowed out out of the container, and it ignited, and it had the fault with the danger of becoming a fire.

[0003] Moreover, in connection with the charge and discharge of a cell, there was a problem on which an opening is generated among two poles, or the positive-electrode matter and the negative-electrode matter produce blinding of a separator with a volume change in a lifting and this slightly, and the capacity and internal resistance of a cell deteriorate.

[0004] Although the so-called polymer battery using the sheet of an ion conductivity polymer as a separator between two poles was developed instead of the organic solvent, since it became inadequate contacting an electrode active material, there was a fault, like the volume of a separator with high internal resistance is needed for an excess.

[0005]

[Problem(s) to be Solved by the Invention] In view of this trouble, even when a cell is damaged, possibility of this invention that an organic solvent will flow out out of a container is small, its safety is high, and there is little degradation accompanying charge and discharge, and it aims at offering a lithium ion battery with a large volume energy density.

[0006]

[Means for Solving the Problem] This invention forms (1) positive electrode and a negative electrode in the front face of a foil-like charge collector, respectively, and rolls them spirally in the condition of having made both countering mutually. Among these both An organic solvent, The manufacturing method of the lithium ion battery which diffuses the electrolyte which contains a lithium in this gel after making the liquid which consists of a gelling agent or its raw material sink in and making this gel, And the electrolyte which forms (2) positive electrodes and a negative electrode in the front face of a

foil-like charge collector, respectively, winds spirally in the condition of having made both counteracting mutually, and contains a lithium among these both. The electrolytic solution which consists of an organic solvent which dissolved this electrolyte, and a gelling agent or its raw material is made to sink in. The manufacturing method, (3) positive electrodes, and the negative electrode of the lithium ion battery which makes this gel are formed in the front face of a foil-like charge collector, respectively. Furthermore, a gelling agent or its raw material is made to exist in a part of separator [at least] between which it is placed between those front faces or two poles. Roll said positive electrode and negative electrode spirally in the condition that you made it counter mutually, make an organic solvent sink in among these both, and said gelling agent or its raw material is dissolved. The manufacturing method of the lithium ion battery which diffuses the electrolyte which contains a lithium in this gel after making this solution gel, And (4) positive electrodes and a negative electrode are formed in the front face of a foil-like charge collector, respectively. Furthermore, the electrolyte which a gelling agent or its raw material is made to exist in a part of separator [at least] between which it is placed between those front faces or two poles, winds spirally in the condition of having made said positive electrode and negative electrode counteracting mutually, and contains a lithium among these both, Make the electrolytic solution which consists of an organic solvent which dissolved this electrolyte sink in, and said gelling agent or its raw material is dissolved. The manufacturing method, (5) positive electrodes, and the negative electrode of the lithium ion battery which makes this solution gel are formed in the front face of a foil-like charge collector, respectively. Furthermore, the gel which consists of an organic solvent and a macromolecule is made to exist in a part of separator [at least] between which it is placed between those front faces or two poles. The manufacturing method of the lithium ion battery which said positive electrode and negative electrode are spirally rolled [lithium ion battery] in the condition that you made it counter mutually, and makes the electrolyte containing a lithium sink in among these both, To a part of separator [at least] between which (6) positive electrodes and a negative electrode are formed in the front face of a foil-like charge collector, respectively, and it is further placed between those front faces or two poles, and an organic solvent, The manufacturing method of the lithium ion battery spirally rolled in the condition of having made the gel which consists of a giant molecule and an electrolyte containing a lithium existing, and having made said

positive electrode and negative electrode countering mutually, And (7) positive electrodes and a negative electrode are formed in the front face of a foil-like charge collector, respectively. It is the lithium ion battery into which the electrolyte which both are spirally rolled in the condition of having countered mutually, and the gel electrolytic solution generated at the thermal polymerization reaction intervenes among these both, and contains a lithium in this gel electrolytic solution, and the organic solvent which dissolved this electrolyte are made to sink.

[0007] Although the approach of (1) does not have the need of taking into consideration active jamming of the polymerization reaction by the electrolyte, and is comparatively wide and it is easy to obtain the gel of a good property, a process becomes complicated and electrolytic impregnation takes long duration. [of the selection range of the class of gel] Although the approach of (2) has the narrow selection range of gel, it can be produced only by changing a little conventional production process, and it is high. [of productivity] (3) And the approach of (4) is effective especially when the raw material solution of a gelling agent is hyperviscosity, and it can do [making the gel of uniform concentration for a short time, or]. (5) And most becomes uniform [the approach of (6) / distribution of gel], and a cell with little dispersion in quality is obtained.

[0008] It is desirable to use a thermal polymerization reaction in respect of the ease of a production process, or the stability of the gel in case of the breakage accident of a product, for example, it dissolves vinylene cull BONATO and azobisisobutyronitril by use ethylene carbonate as a solvent, makes this decompress and sink into the positive electrode matter, the negative electrode matter, and the winding article of a separator, and makes 60 - degreeC and a 20 - hour bulk polymerization reaction perform in nitrogen gas atmosphere mind as a process of the gel electrolytic solution. It generates so that this may be filled up into the detailed hole of the two poles containing ethylene carbonate, and a separator. Then, the gel filled up with between two poles including the electrolyte will be obtained by dipping in the ethylene carbonate solution which melted LiPF₆ of an electrolyte, and making it spread. Moreover, a monomer and a polymerization initiator may be made to dissolve and react to the nonaqueous solvent which dissolved the electrolyte beforehand.

[0009] Being able to control [for example,] the gelation reaction by thermal polymerization easily by controlling the temperature of the assembled cell, the time amount required for the conclusion of a

reaction in the solution polymerization using a vinyl mold monomer and a vinyl mold macro monomer is as follows. A macro monomer is called alias name reactivity oligomer, and the molecular weight is thousands of dalton here. The solubility according to the object and the physical properties of gel are controllable by the design of the various chemical structures. On the other hand, the reactivity of gelation of a macro monomer is almost the same as the reactivity of a monomer, and thermal polymerization is possible for it.

(1) When azobisisobutyronitrile is used as an initiator.

50-degreeC 74-hour 70-degreeC 4.8-hour 100-degreeC When lauryl peroxide is used as a 7.2-minute (2) initiator.

50-degreeC 47.7-hour 70-degreeC 3.5-hour 100-degreeC In this way, since the time amount of gelation is controllable by temperature control, the optimal conditions for a production process can be set up for 3.5 minutes.

[0010] The polymerization reaction which occurs as a device of a reaction as a polymerization reaction used by this invention by branching which consists of a 2 functionality monomer and a polyfunctional monomer by one reaction of an addition polymerization reaction, a polyaddition reaction, a ring-opening-polymerization reaction, and a polycondensation reaction, or generation of a crosslinked polymer can be used suitably.

[0011] Moreover, as a giant molecule which constitutes gel from this invention, the thing containing at least one in polymethylacrylate, a polymethyl methacrylate, a polyacrylonitrile, polystyrene, polyvinyl acetate, Pori cinnamic-acid vinyl, cyclized rubber, polysilane, a polysiloxane, epoxidation polybutadiene, a polyether, polyurethane, polyester, and those copolymers can be used suitably.

[0012] It is desirable for the soluble parameter (δ) of the solvent and macromolecule which constitute gel from this invention to approximate, when obtaining good gel. That is, the function which is a soluble parameter in which it is near or the solvent dissolves a macromolecule in the combination of the same macromolecule and the same solvent is most excellent, and calls such a solvent a good solvent. A good solvent makes max swell gel. The database of a real giant molecule and the soluble parameter of a solvent is completed mostly, and the approach of presuming δ value of the new matter is also established. Therefore, it is possible to look for the organic electrolytic solution which makes max swell gel. The mobility of the lithium ion in the swollen gel is almost equal to the value of only the organic electrolytic solution. Therefore, the ionic conductivity change by

existence of gel can be disregarded by gel / good solvent system. The ratio of the soluble parameter of the macromolecule which constitutes gel, and the organic solvent contained in it is desirable when it obtains good gel that it is within the limits of 1 to 0.7 thru/or 1 to 1.3, and it is more desirable that it is within the limits of further 1 to 0.8 thru/or 1 to 1.2. As an example of a good solvent, when giant molecules are polystyrene ($\Delta=18.7 \text{ MPa}^{1/2}$), a polymethyl methacrylate ($\Delta=18.6 \text{ MPa}^{1/2}$), and polyvinyl acetate ($\Delta=19.6 \text{ MPa}^{1/2}$), the good solvent is a tetrahydrofuran ($\Delta=19.4 \text{ MPa}^{1/2}$) and diethyl carbonate ($\Delta=18.0 \text{ MPa}^{1/2}$).

[0013] After forming gel thinly on the surface of an electrode beforehand, one kind of for example, various acrylate and a methacrylate monomer or the mixture of two or more monomers and a vinylene carbonate monomer is copolymerized as an approach of winding using a DMF solvent by making azobisisobutyronitrile into an initiator, a product is settled with a methanol, and 2 yuan or plural copolymers are obtained by the shape of a solid-state. An organic electrolyte is made to swell and distribute this copolymer, and gel is obtained. This gel serves as a ***** solution in which meeting structure is destroyed and a good fluidity is shown under high shearing stress. On an electrode, a doctor blade is used and this solution is applied in the shape of a thin layer. A paint film returns to the gel state. In this way, it can consider as the cell which winds the made electrode and has the gel electrolytic solution.

[0014] The positive-electrode matter used for this invention and the negative-electrode matter can be suitably chosen according to the military requirement of a cell, for example, use transition metals, such as Mn, nickel, and Fe, as a principal component as positive-electrode matter, and can use desorption and the lithium compound metallic oxide which can carry out *** for a lithium at the time of the charge and discharge which consists of a lithium and oxygen.

[0015]

[Example]

[The first example] LiCoO_2 was applied to aluminium foil, the positive electrode which carried out press working of sheet metal, and the negative electrode which applied graphite to copper foil and carried out press working of sheet metal were spirally rolled through the porous polyethylene layer, and the closed-end cylinder-like cell can was equipped. The monomer mixture which consists of a weight ratio 2 to 1 of a methyl methacrylate monomer and the diaryl carbonate monomer of bisphenol A was dissolved in the mixed organic solvent which consists of

propylene carbonate which dissolved LiPF₆ of 1M, and 1 and 2 dimethoxyethane, it considered as the solution of weight concentration 12%, and the liquid which added 1.5% per monomer AUV for azobisisobutyronitrile in this solution was made to sink in under reduced pressure among these two poles. This was obturated under nitrogen-gas-atmosphere mind, and the lithium ion battery which heats for 30 minutes in 75-degreeC, and has a gel electrolyte was obtained.
[0016]

[The second example] LiCoO₂ was applied to aluminium foil, the positive electrode which carried out press working of sheet metal, and the negative electrode which applied graphite to copper foil and carried out press working of sheet metal were spirally rolled through the separator which consists of a porous polyethylene layer, and the closed-end cylinder-like cell can was equipped. After making the solution which dissolved polystyrene monomer 180g, divinylbenzene 5g, and benzene peroxide 1.5g in tetrahydrofuran 150g sink in under reduced pressure among these two poles, it heated in 60-degreeC in nitrogen-gas-atmosphere mind for 2 hours, and the polymerization reaction was made to perform. This was made to add and swell the solution which dissolved LiPF₆ of 1M in the mixed liquor of ethylene carbonate and dimethoxyethane under nitrogen-gas-atmosphere mind, and it considered as the good gel electrolytic solution, and it obturated and the lithium ion battery was obtained.

[0017]

[The third example] LiCoO₂ was applied to aluminium foil and the liquid which dissolved 100g [of vinyl acetate] and cinnamic-acid vinyl 10g and azobisisobutyronitrile 2g in tetrahydrofuran 150g was made to sink into the positive electrode which carried out press working of sheet metal, the negative electrode which applied graphite to copper foil and carried out press working of sheet metal, and the separator which consists of a porous polyethylene layer under reduced pressure. These were heated for 30 minutes in 60-degreeC under ejection and nitrogen-gas-atmosphere mind from liquid, respectively, and it considered as gel. Thus, the cell can of the shape of winding and a closed-end cylinder was equipped with the positive electrode with which it filled up with the obtained gel all over the opening, the separator, and the negative electrode. Among these two poles, you added the solution which dissolved LiPF₆ of 1M in the mixed liquor of ethylene carbonate and dimethoxyethane under nitrogen-gas-atmosphere mind, and made it spread in gel, and it considered as the good gel electrolytic solution, and it obturated and the lithium ion battery was obtained.

[0018]

[The fourth example] 1g of emulsifiers and 1l. of water containing 1g of potassium persulfate are made to distribute styrene monomer 100g and divinylbenzene 2.5g, it stirs by 60-degreeC for 1 hour, and polystyrene latex is obtained. After freeze-drying this latex and being powdered, the chloroform or dimethylformamide which is the good solvent of polystyrene was distributed, and swelling micro gel was obtained. Sulfur trioxide sulfur performed surface sulfonation (whenever [sulfonation] 0.1 - 15%) for this micro gel. The water after recovery was distributed, micro gel freeze-dried, after neutralizing thoroughly by LiOH, and it obtained micro gel powder. In this way, the obtained surface sulfonation micro gel powder was made to swell with the ethylene carbonate of LiPF₆ of 1M, and a methylethyl carbonate (volume ratio 1:3) solution, it considered as gel, this gel was thinly applied to each front face of a positive electrode, a separator, and a negative electrode, each was rolled spirally in piles, and the closed-end cylinder-like cell can was equipped. This was obturated in nitrogen-gas-atmosphere mind, and the lithium ion battery was obtained.

[0019]

[The fifth example] 1g of benzoyl peroxides was diluted with the 300ml organic electrolytic solution to methacrylate 200g and divinylbenzene 1g, 60 degrees was stirred for C or 3 hours, and the polymer solution was obtained. This was applied in the shape of a thin layer on the surface of two poles, it wound on both sides of the porosity plastics spacer, and the closed-end cylinder-like cell can was equipped. This was obturated in nitrogen-gas-atmosphere mind, and the lithium ion battery was obtained.

[0020]

[The sixth example] LiCoO₂ was applied to aluminium foil, the positive electrode which carried out press working of sheet metal, and the negative electrode which applied graphite to copper foil and carried out press working of sheet metal were spirally rolled through the separator which consists of a porous polyethylene layer, and the closed-end cylinder-like cell can was equipped. Styrene monomer 10ml, acrylate or methacrylate monomer 10ml mixture, and divinylbenzene 1ml were added to 100ml of organic electrolytes, and the solution which mixed dicumyl peroxide 60ml was made to permeate among these two poles. As a result of making a polymerization reaction perform by heat-treating this by 70-degreeC for 3 hours, the solution which permeated turned into a thick polymer solution, and the fluidity reduced it remarkably.

[0021]

[The seventh example] Polyvinyl alcohol 0.5g was dissolved in 30ml of boiling water, it diluted to 500ml the back, styrene monomer 15g, divinylbenzene 2g, and 0.2g of benzoyl peroxides were added to this solution, it stirred in 90-degreeC for 4 hours, and the latex particle was obtained. What was made to swell this particle in a tetrahydrofuran, was made to distribute with the organic electrolytic solution, and was made into the shape of a slurry was applied and wound around the front face of the two poles of a lithium ion battery, and it considered as the cell.

[0022]

[Effect of the Invention] The breakdown test (it **** and examines) which puts a nail and is crowded from the side face of a cylinder-like cell about the cell created in the first thru/or the fourth example was performed. As the situation in that case was shown in a table 1, by the cell made by the approach of this invention, it was not admitted whether having been very small, but to this, the electrolytic solution flowed out and generating of flame became an electrolyte with big flame by the cell not using gel.

[0023]

[A table 1]

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[0024] After carrying out impregnation of the electrolytic solution to the winding article of two poles according to this invention a passage clear from the above explanation, By carrying out impregnation of the electrolyte to the gel which the gel which made this electrolytic

solution gel or contained the electrolytic solution on the surface of two poles is made to exist, and winds, or exists in the winding article of two poles. In order that there may almost be no runoff of the electrolytic solution at the time of the container of a cell being damaged, it excels in safety, and a lithium ion battery also with little degradation accompanying charge and discharge is obtained, and it is very useful on industry.

[Translation done.]
